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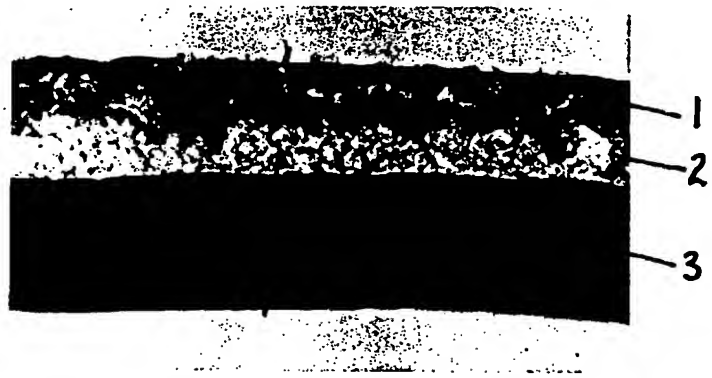
(54) Ink jet recording medium and printing method

(57) Protected ink jet images on a recording medium are produced by

1) printing on to a receiving medium which comprises a substrate coated with at least one ink receiving layer and at least one upper protective layer which comprises polymeric particles having film forming temperatures between 60 to 140°C, preferably between 100 to 120°C, and at least one binder, and

2) subsequently heating the printed image to form a stable image protecting coating.

The printed image is sealed by heat, preferably, by passing through a laminator. The protective layer is receptive to inks during printing and provide high quality images of good colour strength. The image is substantially retained within the upper protective layer following heating and fusion of the particles to provide a protective cover.



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Description

[0001] This invention relates to a recording medium for ink jet recording and to the treatment of images prepared by an ink-jet printing process.

[0002] Ink jet printing is a non impact printing method that in response to a digital signal produces droplets of ink that are deposited on a substrate to produce an image. Ink jet printing has found broad application in industry as well as for output from personal computers in the home and office. There is increasing interest in the use of digital imaging with ink jet printers as an alternative to conventional photographic imaging techniques. However the images produced by ink jet printers are seen as suffering several disadvantages when compared with conventional photographic images. In general they lack the overall quality of photographic images, look and feel substantially different, lack stability to light, and are more sensitive to water, scratching, rubbing, and environmental influences.

[0003] Aqueous inks are commonly used in ink jet printers for environmental and safety reasons, particularly those intended for use in the home or office. However sensitivity of the printed image to water is a particular problem where aqueous inks are used.

[0004] One way of overcoming these disadvantages is to laminate or encapsulate ink jet images, particularly those destined for external display. By lamination is meant the combination of a printed ink jet receiving layer with a transparent overlay, this combination usually being accomplished with an adhesive activated by heat, pressure, or both. The overlay acts as a physical protection for the image and completely seals it from ingress of water. By encapsulation is meant the combination of a printed ink jet receiving layer between two laminating sheets, that on the image surface being transparent, the combination being accomplished with an adhesive activated by heat, pressure, or both. Encapsulation is most effective if the laminating sheets extend beyond the ink jet image and are bonded to each other at the extremities, thus preventing ingress of water through exposed edges of the ink jet image.

[0005] However lamination and encapsulation both have disadvantages. They are expensive because additional materials are required together with additional handling and equipment. Moreover residual solvents such as the organic cosolvents which are frequently incorporated with aqueous inks remain trapped with the printed image, and these can sometimes degrade image quality by causing stain or migration of the image on storage or exposure. In addition the material of the laminate or adhesive can also deteriorate and cause stain on exposure. Laminates do not always adhere well to printed ink jet images, and adhesion can depend on the coatings of the ink receiving layer, the amount and type of solvent in the ink, and also on the quantity of ink laid down. This is particularly found when the ink jet image is being used instead of a conventional photographic image, as heavy ink loads are often used to reproduce the image quality.

[0006] As an alternative to lamination, various additional coatings and treatments for ink jet receiving layers have been proposed. In most cases these are coatings such as lacquers or varnishes which have to be applied after printing the image, thus also requiring additional equipment. For instance GB-A-2 337 482 discloses a method for increasing the rub resistance of an ink jet image by coating or over-printing the image with an aqueous solution of a styrene acrylate polymer.

[0007] Various types of ink jet receiving materials are also known wherein the top layer or an upper layer of the material comprises a film forming polymer and the lower layer or layers comprise ink receiving layers, such that when the image is printed the ink passes through the upper layer or layers and is held by the lower layers. The material is subsequently heated above the film forming temperature of the polymer, which thus fuses to form a barrier layer which seals the image. Such heat sealing systems are disclosed for instance in JP-A-59/222381, 07/237348, 08/02090, and 09/104164 and in EP-A-0 858 905 and 0 858 906. This method is limited, however, as a high temperature is necessary to melt the polymer (170°C in the Examples of EP-A-0 858 906), and special equipment is required to achieve this. Moreover not all substrates and ink receiving layers can withstand the high fusing temperature, and this restricts the generality of these methods. In addition the resultant image retains the solvents and can be subject to deterioration in the same fashion as a laminated or encapsulated image.

[0008] There is thus still a need for a convenient and general method for protecting ink jet images. We have found such a method.

[0009] According to the present invention there is provided an ink jet printing method which comprises the steps of:-

1) printing on to a receiving medium which comprises a substrate coated with at least one ink receiving layer and at least one upper protective layer which comprises polymeric particles having film forming temperatures between 60 to 140°C, preferably between 100 to 120 °C, and at least one binder, and

2) subsequently heating the printed image to form a stable image protecting coating.

[0010] In contrast to the materials previously known in the art, the image in the materials of this invention is substantially retained within the upper protective layer. It is believed, however, that any retained solvents are held in the lower image receiving layers, thus separating them from the colorant.

[0011] The protective layers of the invention are receptive to inks during printing, give high quality images of good colour strength, adhere well after printing and

fusing, provide a high level of scratch and rub resistance to the final image even when wet, and maintain the same level of flexibility as the rest of the assembly.

[0012] Suitable substrates to carry the layers of the invention include any of those commonly used for ink jet receiving media, for example paper, high wet-strength paper, label grade paper, treated paper such as pigment, resin or polyethylene coated paper, transparency materials, synthetic papers, fabrics, transfer materials, and polymeric substrates such as cellulose acetates, polyesters, poly(propylene), and poly (vinyl chloride).

[0013] Suitable ink receiving layers include any of those commonly used in ink jet media, particularly those employing at least one binder such as gelatin, poly (vinyl alcohol), poly (vinyl pyrrolidone), carbohydrates such as gums, treated carbohydrates such as hydroxyethyl cellulose or carboxymethyl cellulose, acrylic polymers, or mixtures of such binders. Such ink receiving layers are well known in the art. Preferably the ink receiving layer comprises poly (vinyl alcohol) having a degree of hydrolysis of at least 88% as binder. It is to be understood that the ink receiving layers for the materials of this invention may advantageously include additives which are commonly employed in ink jet receiving layers such as inorganic pigments or fillers such as silica, alumina, clays, and calcium carbonate, dye fixing agents such as cationic polymers, surfactants, cross linking agents, optical brighteners, and light stabilisers.

[0014] Suitable binders for the upper protective layer include poly (vinyl alcohol), copolymers of poly (vinyl alcohol), gelatin, poly (vinyl pyrrolidone), carbohydrates such as gums, treated carbohydrates such as hydroxyethyl cellulose or carboxymethyl cellulose, acrylic polymers, or mixtures of such binders. A preferred binder is poly (vinyl alcohol) which has a degree of hydrolysis of at least 90%, and a particularly preferred binder is poly (vinyl alcohol) which is about 99% hydrolysed. This is hereinafter referred to as 99% PVA.

[0015] A suitable particle size for the polymeric particles is between about 1 μm and about 50 μm, with a particle size between about 5 μm and about 20 μm being preferable. Suitable polymers for the polymeric particles include low density polyethylene and copolymers of ethylene with other ethylenically unsaturated monomers, such as ethylene-acrylic acid copolymers. A particularly suitable particulate polymer comprises low density polyethylene spherical beads having an average diameter of about 12 μm. Another particularly suitable particulate polymer comprises spherical beads of a 7% acrylic acid/ polyethylene copolymer having an average diameter of about 10 μm. These polymers have film forming temperatures of 105-107°C. As described on page 489 in the book Emulsion Polymerisation and Emulsion Polymers (edited by P.A. Lovell and M.S. El-Asser published by John Wiley and sons in 1997) the film forming temperature represents the minimum temperature at which a latex dispersion will form a film.

[0016] A suitable coating weight for the upper protective layer is from about 15 to about 40 gm^{-2}. A preferred coating weight is between about 25 and about 30 gm^{-2}.

[0017] The upper protective layer may optionally also comprise additives such as surfactants to improve coating quality and cross linking agents such as aldehydes, boric acid, divalent metallic cations and the like.

[0018] The image receiving materials of the invention may be prepared by simultaneously coating the image receiving layer or layers together with the upper protective layer on to the substrate. Alternatively the upper protective layer may be coated on to a existing ink jet medium which comprises the substrate and image receiving layers. The upper protective layers of the invention are particularly suitable for this second aspect as they may be coated as aqueous formulations which give good adhesion to the image receiving layer.

[0019] According to one aspect of this invention, the printed image is heated by passing through a laminator. By laminator is meant a device which is normally used for the lamination of printed images which comprises a means of heating and pressing together the image and the laminating sheet thus causing the two to adhere, commonly by passing them through heated rollers. This aspect is particularly preferable because many printing and processing houses already possess and use laminators which can be applied to the materials of this invention. However the advantage of this invention is that the additional expensive lamination sheet is unnecessary. Alternatively the heating process may use any other convenient method, such as heated air or infra red or microwave radiation.

[0020] According to another aspect of the invention, the printed image is heated by passing through a laminator in conjunction with a second, inert sheet which is held against the image protective layer of the material. The inert sheet does not adhere to the material, but protects it from the rollers of the laminator, and may be used to impart a high gloss or other desired appearance such as an embossed pattern or security symbol to the final image by suitable choice of the inert sheet. The inert sheet may then be recycled. Suitable inert sheets include release papers or liners such as silicone release liners, casting films and papers, and polyester films.

[0021] The materials of the invention may be printed using any convenient ink jet printer, for example a continuous printer or a piezoelectric or thermal drop-on-demand printer. Suitable jetting inks include aqueous inks and those based on organic solvents such as 2-butanone (MEK), ester solvents, and mineral oils. Suitable colorants for these inks include dyes or pigments. Preferred inks for the invention are pigmented aqueous inks.

[0022] The following Examples will serve to illustrate the invention but are not meant to be limiting in any sense:-

Example 1

[0023] A formulation was prepared using the following components:-

99% PVA 10% solution	10.0g
Silicone surfactant	0.25g
Ethylene acrylic acid copolymer beads	5.0g
Deionised water	4.75g

[0024] This formulation was coated on to a commercially available ink jet receiving medium which has a poly (vinyl chloride) substrate coated with a receiving layer comprising poly(vinyl alcohol)/ poly(vinyl acetate), silica, and a carbohydrate gum. The coating weight of the upper protective layer is 29 gm^{-2}. A test pattern was printed with pigmented inks using an Epson 200 printer, allowed to dry, and the coating was sealed by passing it through a GBC 1200 laminator at a heat setting corresponding to a temperature of 120°C with the image face contacted with a smooth inert cover sheet. A clear glossy image was produced, resistant to wet rubbing, and the cover sheet was recovered for reuse.

Example 2

[0025] A receiving layer was prepared as in Example 1. This was printed on a Novajet III printer and sealed using a Seal Image 600 laminator. A bright image was produced, resistant to smudging when rubbed with a thumb despite a high ink loading.

Example 3

[0026] A receiving layer was prepared as in Example 2. It was printed with a test chart and the image was sealed as in Example 2. The black areas of the image possessed 100% density of yellow, magenta, and cyan inks. A photomicrograph of a selected black printed area in cross section is shown in the accompanying drawing, wherein 1 denotes the upper protective sealed layer, 2 the lower receiving layer and 3 the poly(vinyl chloride) base. The cross section was prepared using a microtome, and it can be seen that substantially all of the black image is located in the top sealed layer 1.

Example 4

[0027] A coating solution was prepared as follows:-

[0028] 12.5g of polyethylene beads were mixed with 12.5g of a 5% solution of Olin 10G surfactant and warmed to 40°C. 6.25g of a 10% solution of a high isoelectric point gelatin was added, and the mixture made up to 50ml with water and dispersed with ultrasound for 5 minutes. This solution was coated and printed as in Example 2.

Example 5

[0029] A formulation was prepared using the following components:-

98% PVA 7.5% solution	40.0g
Triton X100 surfactant 3% solution	20.0g
Polyethylene beads	20.0g
Deionised water	20.0g

[0030] Triton X100 is a non-ionic wetting agent based on octylphenol ethoxylate (ave. 9 to 10 moles ethylene oxide). The supplier is Union Carbide Chemicals and Plastics Company Inc., Danbury, CT, USA.

[0031] This formulation was coated on to a commercially available ink jet receiving medium, Ilford UM2GP6, which has a substrate comprising a paper core coated on each side with a layer of polyethylene, the face side of which is coated with a receiving layer comprising a mixture of swelling polymers The coating weight of the upper protective layer is 36 gm^{-2}. A test pattern was printed with aqueous dye-based inks using an Epson 800 printer, allowed to dry, and the coating was sealed by passing it through a Seal Image 400 laminator at a heat setting corresponding to a temperature of 118°C with the image face contacted with a smooth sheet of polyester film. A clear glossy image was produced which was resistant to wet rubbing.

[0032] Finally, it is understood that variations and modifications from the examples given herein are possible in view of the foregoing disclosure. Therefore, although the invention has been described with reference to certain preferred embodiments it will be appreciated that other ink receiving layer and protective layer materials may be used.

Claims

1. A recording medium for ink jet printing comprising:

   a substrate coated with at least one ink receiving layer; and
   at least one protective layer, wherein said protective layer is on top of said ink receiving layer and characterised by comprising a particulate polymer having film forming temperature between 60 and 140°C and a binder.

2. A recording medium according to Claim 1, wherein the substrate is a paper, transparency materials, fabric, transfer material or polymeric substrate.

3. A recording medium according to Claim 1, 2 or 3, characterised in that the ink receiving layer includes at least one binder selected from gelatin, poly(vinyl

alcohol), poly(vinyl pyrrolidone), carbohydrates, gums, treated carbohydrates, hydroxyethyl cellulose, carboxymethyl cellulose, acrylic polymers, and mixtures thereof.

4. A recording medium according to claim 3, characterised in that the ink receiving layer comprises poly (vinyl alcohol) having a degree of hydrolysis of at least 88%.

5. A recording medium according to any one of Claims 1 to 4, characterised in that the ink receiving layer further includes one or more additives selected from inorganic pigments, fillers, silica, alumina, clays, calcium carbonate, dye fixing agents, cationic polymers, surfactants, cross linking agents, optical brighteners and light stabilizers.

6. A recording medium according to any one of Claims 1 to 5, characterised in that the particulate polymer has a particle size between 1 and 50μm.

7. A recording medium according to any one of Claims 1 to 6, wherein the particulate polymer is selected from low density polyethylene and copolymers of ethylene with ethylenically unsaturated monomers.

8. A recording medium according to Claim 7, wherein the ethylenically unsaturated monomers comprise acrylic acid.

9. A recording medium according to any one of Claims 1 to 8, characterised in that the particulate polymer comprises low density polyethylene spherical beads having an average diameter of approximately 12μm.

10. A recording medium according to any one of Claims 1 to 8, characterised in that the particulate polymer comprises spherical beads of a 7% acrylic acid/polyethylene copolymer having an average diameter of approximately 10μm.

11. A recording medium according to any one of Claims 1 to 10, characterised in that the protective layer has a coating weight from 15 to 40 gm^{-2}.

12. A recording medium according to any one of Claims 1 to 11, characterised in that the protective layer further comprises additives selected from the group consisting of surfactants, cross linking agents, aldehydes, boric acid and divalent metallic cations.

13. An ink jet printing method comprising the steps of:

1) printing on to a recording medium according to any one of the preceding Claims, and

2) heating the printed image to form a stable image-protecting coating.

14. A method according to Claim 13, characterised in that the printed image is heated under pressure to form the protective coating.

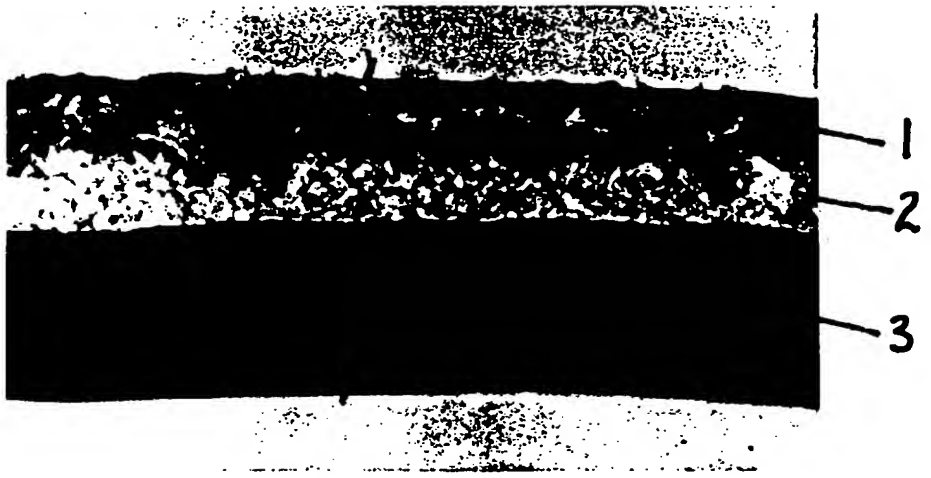
15. A method according to Claim 13 or 14, characterised in that the printed image is heated by passing through a laminator.

16. A method according to Claim 15, wherein an inert sheet is brought into contact with said protective layer prior to passing the printed recording medium through the laminator.

17. A method according to Claim 16, wherein the inert sheet is a release paper or liner, a silicone release liner, casting film, casting papers, and polyester films.

18. A method according to Claim 17, wherein the surface of the inert sheet is adapted to impart a high gloss, embossed pattern or security symbol to the final image.

19. A method according to any one of Claims 13 to 18, characterised in that the inks used to print the image on the receiving layer are aqueous inks or inks based on organic solvents.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